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Vibrational Spectroscopy of the Electrode-Electrolyte  
Interface. Use of Fourier Transform Infrared Spectroscopy.

by

T. Davidson, B. Stanley/Pons, A. Bewick, and P. Schmidt

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Vibrational Spectroscopy of the Electrode-Electrolyte Interface.


Use of Fourier Transform Infrared Spectroscopy.

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The power of electrochemically modulated infrared reflectance spectroscopy (EMIRS) for the elucidation of mechanisms of surface catalyzed reactions at an electrode surface has recently been demonstrated (1-4). We have now successfully used a Fourier transform infrared instrument to obtain spectra under similar conditions. Although the absolute sensitivity is less than that of EMIRS, the speed, spectral range and versatility of FTIR will make it an indispensable tool for the study of electrode solution interfaces. In this initial study, the structure of acetonitrile in the double layer at a platinum electrode was investigated, as well as the effect on that structure of commonly used cations (lithium and tetrabutylammonium). Recent (5) electrochemical investigations have indicated that acetonitrile is strongly adsorbed at a polycrystalline platinum surface over a wide range of potentials. That work also pointed out the non-interference of lithium cation on the strength of this adsorption. Others (6) have indicated, however, disruption of solvent adsorption by specific adsorption of tetrabutylammonium ion. There have also been indications (7) that the water concentration in the interfacial region is affected by these cations. The experiment was designed to see if any of these effects could be sensed with infrared absorption changes at various electrode potentials.

The FTIR spectra were recorded between 4000 and 650  $\text{cm}^{-1}$  on a Nicolet 7199 instrument fitted with a polariser. The cell (described elsewhere (8)) had a circular plate window (40 mm diameter; 2mm thickness). The platinum indicating electrode was a disk (1.1  $\text{cm}^2$ ) mounted in the end of a Kel-F rod, and was

polished to a mirror finish by 0.05 micron alumina. The counter electrode was a platinum wire, and the reference was an  $\text{Ag}/\text{Ag}^+$  (0.01 M) in acetonitrile containing the same electrolyte as the solution under investigation.

### Results and Discussion

The difference spectra obtained using "anhydrous" acetonitrile containing (a) 0.1 M lithium perchlorate and (b) 0.1 M tetrabutylammonium fluoroborate are shown in Figure 1 for a potential step experiment from 0.00 V to 2.00 V vs the  $\text{Ag}/\text{Ag}^+$  reference. The spectrum from the lithium perchlorate solution clearly shows the appearance of a  $\text{C}\equiv\text{N}$  stretch band at  $2325\text{ cm}^{-1}$ . This band is strongly shifted from the  $\text{C}\equiv\text{N}$  stretch for bulk acetonitrile and it corresponds to the formation of a new species at 2.0 V, oriented to give the  $\text{C}\equiv\text{N}$  band a component perpendicular to the electrode surface as would be expected for bonding to the surface via the nitrogen. Little or no  $\text{CH}_3$  stretch is observed indicating little perturbation of this part of the molecule. Also noted is the band near  $1650\text{ cm}^{-1}$ , the water bending region, indicating perturbation of the residual water in the interfacial region. The magnitude and shape of this band is strongly dependent on the amount of water present in the system and there is also a broad feature in the corresponding OH stretch region. In the case of tetrabutylammonium tetrafluoroborate the spectrum is very different. In the  $\text{C}\equiv\text{N}$  stretch region, there is a broad feature on which is superimposed a sharp band, at exactly the bulk acetonitrile position, but of opposite sign to

that of the C≡N band for the lithium perchlorate solution. It would appear, therefore, that there is a small decrease in the amount of acetonitrile present in the double layer at the more positive potential. In all cases, there is also a strong band near  $1200\text{ cm}^{-1}$  and work is continuing to identify its origin.

If acetonitrile- $\text{d}_3$  is substituted for acetonitrile in the above experiments, the results are similar. Figure 2 represents the spectrum obtained between 0.00 and 2.50 V using lithium perchlorate in the deuterated solvent.

Experiments performed over a range of electrode potentials show that acetonitrile or acetonitrile- $\text{d}_3$  adsorbed onto the surface of the platinum electrode from perchlorate solutions gives an almost normal vibrational spectrum when the electrode potential is not far removed from  $E_{\text{pzc}}$ . However, with more extreme conditions of high positive potentials, the C≡N stretching frequency is strongly blueshifted (Figure 3). A shift in this direction is interesting and is indicative of the bonding of the molecule to the surface. Red-shifting is commonplace in molecules with polarizable bonds which form adducts and complexes with strongly electronegative species (9,10). The blue-shifting which occurs in acetonitrile, however, is entirely consistent with the behaviour of this molecule as a Lewis base. It has been known for some time that the C≡N stretch in acetonitrile is blue-shifted upon the formation of adducts with a variety of Lewis acids. This blueshifting, however, is not substantially influenced by the formation of an adduct bond. Purcell and Drago (9) showed that the kinematic coupling of the C≡N and N-acid

bonds can, at best, account for about  $10\text{ cm}^{-1}$  of the increase in the vibrational frequency. These authors determined that the major contribution to the blue-shift occurred through the strengthening of the  $\text{C}\equiv\text{N}$  bond. And, in particular, they found that although the adduct may lead to a slight decrease in the strength of the  $\pi$ -bonding system, the increase in strength in the  $\sigma$ -bond between C and N more than compensated any effects of polarization. Thus, the  $\text{C}\equiv\text{N}$  stretching force constant is increased simply because the strength of the bond is increased.

Similar conclusions were reached by Sadlej and Kecki (10). Purcell and Drago (9) based their analysis on calculations using the extended Huckel method. Sadlej and Kecki (10) made use of a modified CNDO scheme. In both sets of analyses it was possible to choose two  $\pi$  orbitals and one  $\sigma$  orbital as being responsible for the majority of the bonding between C and N in acetonitrile. Furthermore, both sets of authors concluded that in the presence of an adduct a certain level of re-hybridization occurs on the N atom. In particular, Sadlej and Kecki state that the  $2p\sigma$  and  $2s$  atomic orbitals on nitrogen essentially describe the lone-pair orbital on nitrogen. The formation of the complex with a positively charged Lewis acid appears to increase the  $2p\sigma$  character of the lone-pair molecular orbital. At the same time, there appears to be a more pronounced  $2s_{\text{N}}$  participation in the formation of the  $\text{C}\equiv\text{N}$   $\sigma$  bond. The strength of the bond is observed to increase under these conditions.

It is interesting to note that the location of the shifted  $\text{C}\equiv\text{N}$  vibrational stretch is potential-dependent, Figure 3. Again,



this observation is entirely consistent with that which is known from the behaviour of acetonitrile in the free, solution phase. The potential dependence of the frequency for the adsorbed acetonitrile reflects the fact that a variety of electronegative adducts lead to the same behaviour for acetonitrile in the solution phase.

It is apparent from these initial experiments that a standard FTIR instrument may be used quite effectively in the investigation of electrochemical interfacial phenomena. Work is in progress to increase the sensitivity of the technique and to apply it to aqueous systems.

### Acknowledgements

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## References

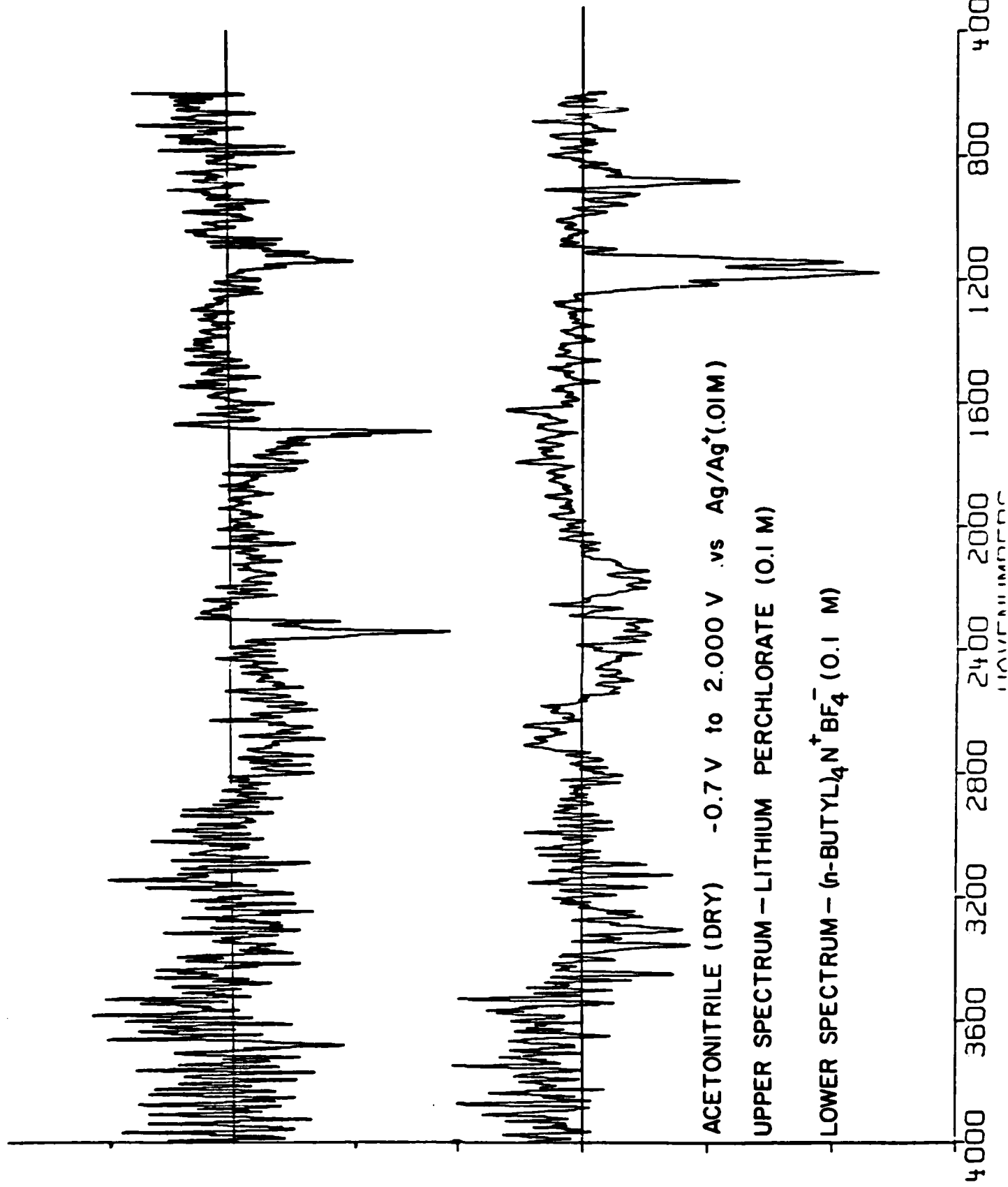
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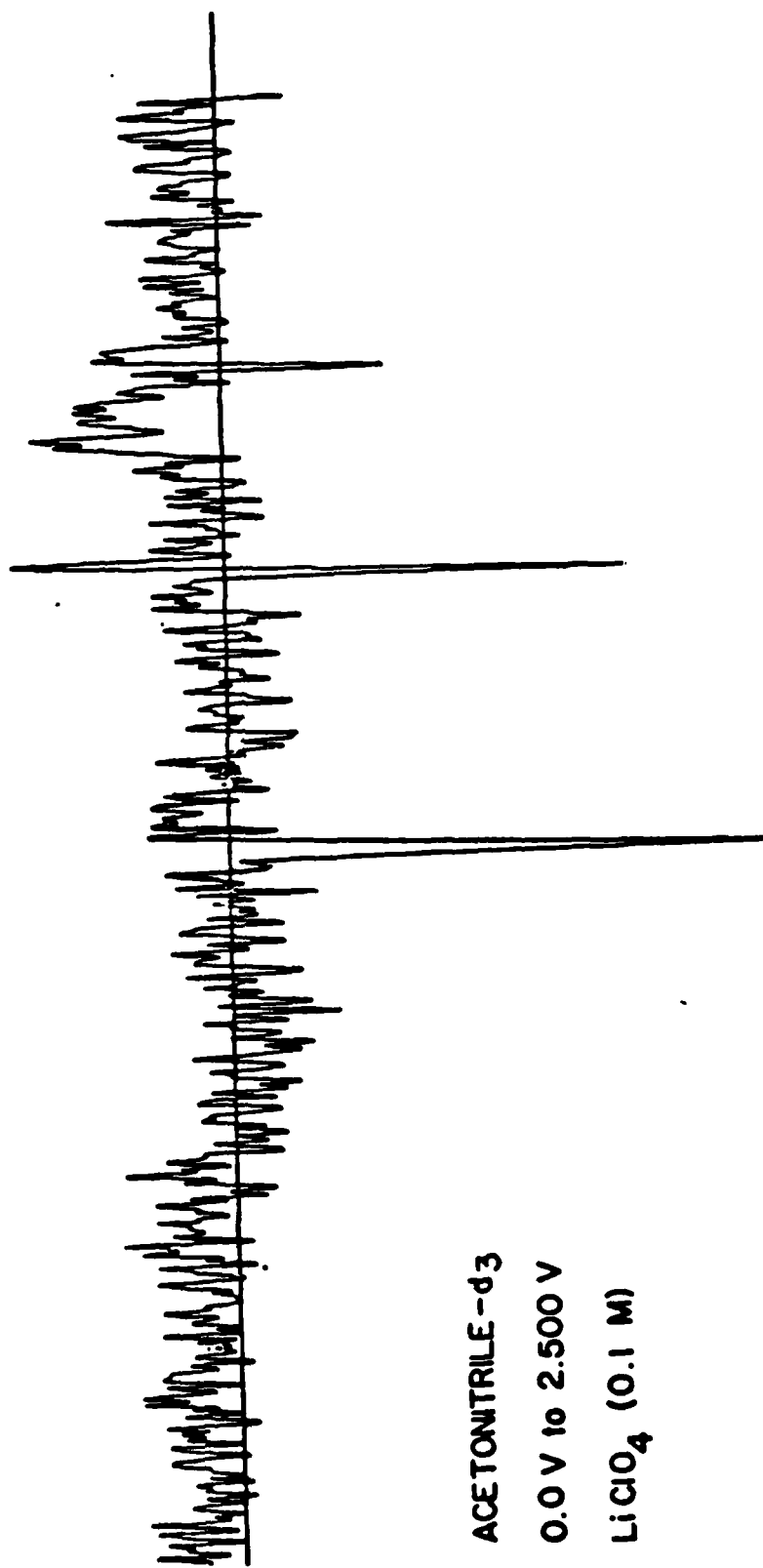
### Figure Legends

Figure 1. FTIR spectra of the Pt/CH<sub>3</sub>CN interface.

Figure 2. FTIR spectra of the Pt/CD<sub>3</sub>CN interface.

Figure 3. C≡N vibrational fundamental location for acetonitrile (AN) and acetonitrile-d<sub>3</sub> (DAN) as a function of potential.





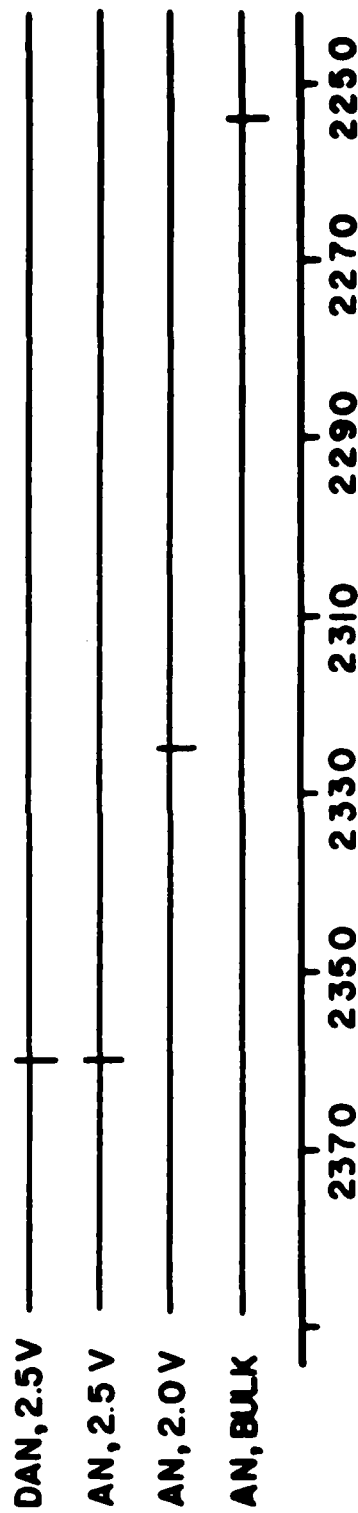
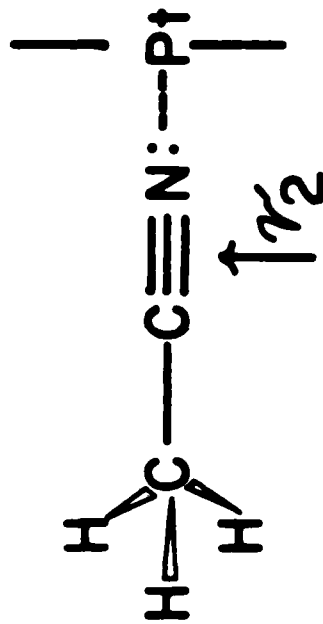
ACETONITRILE-d<sub>3</sub>

0.0 V to 2.500 V

LiClO<sub>4</sub> (0.1 M)

4000 3600 3200 2800 2400 2000 1600 1200 800 400

Wavenumber (cm<sup>-1</sup>)



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